Preparation, Spectral and Thermal Properties of Dicyanoargentates of Copper and Nickel with Bipyridine

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Coordination compounds $[Ni(bipy)_3]_2[Ag(CN)_2]_3Cl \cdot 9H_2O$ (NB3AH), $[Ni(bipy)_2][Ag(CN)_2]_2 \cdot H_2O$ (NB2AH), and $[Cu(bipy)_2][Ag(CN)_2]_2 \cdot H_2O$ (CB2AH), respectively, have been prepared and identified by elemental analysis, infrared and electron spectroscopy. Thermal stability and stoichiometry of thermal decomposition were studied by using a derivatograph. The intermediates of thermal decomposition were identified by IR spectroscopy and X-ray powder diffractometry. The results indicate that the thermal stability increases in the order NB3AH, CB2AH, NB2AH.

One-dimensional (1D) coordination compounds containing paramagnetic ions linked by appropriate bridging species are intensively studied at present because they exhibit interesting magnetic properties [1]. Dicyanoargentate anion due to its rigidity is suitable bridging species for linking paramagnetic ions as it was observed *e.g.* in $Cu(en)_2Ag_2(CN)_4$ [2]. Dicyanoargentate anion in its coordination compounds beside bridging function can also act as a terminal ligand [3—5], or simply as a counterion balancing the positive charge of the cation [6]. Relatively common are compounds in which dicyanoargentate anions exhibit simultaneously two different structural functions. This is the case of $[Cd(N\text{-Meim})_4\{Ag(CN)_2\}][Ag(CN)_2]$, where N-Meim is N-methylimidazole [7].

We are interested in the study of preparation, crystal structure, magnetic, spectral, and thermal properties of cyano complexes crystallizing from the systems $M—L_N—Ag(CN)_2^-—H_2O$ (M(II) = Ni, Cu; L_N is an N-donor ligand). Thus, from the systems where L_N = bipyridine crystallized compounds $[Ni(bipy)_3]_2[Ag(CN)_2]_3Cl \cdot 9H_2O$ (NB3AH), $[Ni(bipy)_2][Ag(CN)_2]_2 \cdot H_2O$ (NB2AH), and $[Cu(bipy)_2][Ag(CN)_2]_2 \cdot H_2O$ (CB2AH). In our previous papers we have described the crystal structures of the first [6] and the third compound [8]. The structure of NB3AH is formed of $[Ni(bipy)_3]^{2+}$ complex cations, $[Ag(CN)_2]^-$ and Cl^- anions, and water molecules. The water molecules along with the anions with the help of hydrogen bonds form hydrophilic part of the structure which encloses hydrophobic $[Ni(bipy)_3]^{2+}$ complex cations. On the other hand, the structure of CB2AH is built up of *cis*-$[—CN—Cu(bipy)_2—NC—Ag—]^{n+}$ zig-zag chains, isolated $[Ag(CN)_2]^-$ anions, and noncoordinated water molecules of crystallization. The study of magnetic properties of CB2AH indicated its magnetically 2D character with low values of exchange coupling constant J and a long-range ordering in the millikelvin temperature region [9]. In this paper we describe preparation, spectral and thermal properties of the title compounds.

EXPERIMENTAL

All compounds used for syntheses, *i.e.* $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $AgNO_3$, KCN, bipyridine, and ethanol were of anal. grade.

The ethanolic solutions (96 %) of $NiCl_2$, $CuCl_2$, and bipyridine exhibit concentration $c = 0.5$ mol dm^{-3} and water-ethanolic solution of $K[Ag(CN)_2]$ ($\varphi_r = 0.2$) has $c = 0.5$ mol dm^{-3}. The complex compounds were prepared by mixing of nickel (copper) chloride and bipyridine solutions in mole ratios 1 : 2 and 1 : 3, respectively, followed by addition of the formed solution to the solution of $K[Ag(CN)_2]$. The M(II) : $[Ag(CN)_2]^-$ mole ratio was 1 : 2. From these systems complexes NB3AH, NB2AH, and CB2AH, respectively were separated. Compounds NB3AH and CB2AH were recrystallized from water—ethanol φ_r = 1 : 1 mixture. The formed crystals were filtered off, washed with water and dried on air. The complex NB2AH separated as a crystalline powder and was insoluble in water and ethanol. The product was filtered off, washed with water and air-dried.

The prepared complexes were analyzed for the content of carbon, hydrogen, and nitrogen on automatic analyzer Erba. The metal contents after mineralization of the samples were estimated by atomic absorp-

tion spectrometry and chlorine content in NB3AH was estimated gravimetrically as AgCl.

Infrared spectra of the prepared compounds as well as of the intermediates of thermal decomposition were recorded on a Specord M-80 (Zeiss, Jena) spectrophotometer in the range $\tilde{\nu} = 200$—4000 cm^{-1} using KBr pellets technique.

Electronic spectra of the prepared complexes were taken in the solid state on a Specord M-40 (Zeiss, Jena) spectrophotometer in the range $\tilde{\nu} = 11\,000$—50 000 cm^{-1} using $BaSO_4$ as standard.

Thermal measurements were performed with an OD 102 (MOM) derivatograph in ceramic crucibles under dynamic conditions with the following parameters: sample mass 100 mg, TG 100, DTA and DTG 1/5, heating rate 5 °C min^{-1}, air atmosphere, as standard aluminium(III) oxide was used. The intermediates of thermal decomposition were obtained by heating of the samples on the derivatograph followed by cooling or by heating at constant temperature in an electric furnace.

X-Ray powder diffraction patterns of the products and intermediates of thermal decomposition were measured on a Mikrometa 2 (Chirana) diffractometer using Ni-filtered CuK_α ($\lambda = 0.15418$ nm) radiation.

RESULTS AND DISCUSSION

The results of the elemental analyses are in good agreement with the calculated values and confirm the composition of the prepared complexes (Table 1). The presence of chloride anion in the complex NB3AH can be explained by using of nickel chloride as starting material.

The measured infrared spectra of the studied complexes proved the presence of cyano groups, bipyridine, and water (Table 2). Sharp absorption band due to stretching vibration of the cyano groups is very characteristic of cyano complexes. In the spectrum of ionic KCN this band is observed at 2080 cm^{-1} [10]. After its coordination the position of this band is shifted to higher values of wavenumbers. In the spectrum of solid $K[Ag(CN)_2]$ (terminal cyano groups) this band is at 2140 cm^{-1}, while in the spectrum of AgCN (bridging cyano groups) this band is shifted to higher value of 2164 cm^{-1} [11]. In this region the spectrum of NB3AH displays only one absorption band at 2136 cm^{-1}, which is in line with the ionic structure of this compound [6]. This band can be assigned to the asymmetric stretching vibration of the cyano group. In the spectra of NB2AH and CB2AH two absorption bands of the ν(CN) type were observed indicating the presence of terminal as well as bridging cyano groups. These observations are in line with the known crystal structure of CB2AH [8] and suggest the existence of similar structure in NB2AH. The presence of the Ag—C bonds was proved by absorption bands observed in the region of 384—392 cm^{-1} [12].

Table 1. Results of Elemental Analyses of Individual Complexes

Complex	w_i(calc.)/% w_i(found)/%					
	C	H	N	Cl	Ag	M
NB3AH	45.77	3.84	14.56	2.05	18.69	6.78
	45.19	3.66	14.40	1.81	17.95	6.63
NB2AH	40.66	2.56	15.81	–	30.43	8.28
	40.50	2.54	15.59	–	30.82	8.03
CB2AH	40.39	2.54	15.70	–	30.23	8.90
	39.58	2.41	14.96	–	30.67	9.13

Table 2. Infrared Spectra of Complexes ($\tilde{\nu}$/cm^{-1})

Complex			bipy [13]		Assignment
NB3AH	NB2AH	CB2AH			
3520	3560	3560			ν(O—H)
3480	3520	3520			
3116	3114	3112	3086	3160	ν(C—H)
3088	3105	3106	3078	3132	
3072	3098	3080	3061	3096	
3056	3072	3050	3054	3064	
3028	3056	3036		3008	
3034	3020			2984	
2923	3014			2950	
2850					
2136	2168	2168			ν(C≡N)
	2128	2128			
1644	1630	1650			δ(O—H)
1600	1600	1600	1579	1576	ν(C=C)
1562	1572	1564	1553	1560	ν(C=N)
1496	1496	1496			
1472	1472	1472	1448	1452	ν(C—C)
1440	1440	1440	1401	1416	ν(C—N)
1312	1312	1320			
1280	1275	1275	1270		
1248	1248	1248	1248	1248	
1220	1220	1220	1210	1220	δ(CCH)
1165	1176	1176			
1156	1152	1156	1138	1136	
1104	1104	1104	1090	1088	
			1083		
1064	1064	1064	1063	1064	
1044	1044	1044	1039	1040	γ(C—H)
1022	1024	1024	991	992	breathing
896	888	888	890	890	
772	768	766	753	760	γ(C—H)
736	736	732	738		
			710		
656	652	656	651	656	δ(CCC)
632	632	630	618	616	
440	440	440			δ(MCN)
408	416	416	398	400	τ(C—C),τ(C—N)
392	390	384			ν(Ag—C)
284	280	284			ν(M—N)

The presence of bipyridine as ligand in the studied compounds is indicated by several absorption bands. As characteristic can be considered bands arising from the ν(CH) stretching vibrations, which are situated in the region 2850—3112 cm^{-1}. Four absorption bands due to this type of vibration are given for the noncoordinated bipyridine molecule in the paper [13], but due to the symmetry of this molecule (C_{2v}) eight ν(CH) stretching vibrations (four of the type A_1 and four of the type B_2) have to be active in the IR spectrum. We were successful in measuring the positions of all eight absorption bands; these are given in Table 2. In the spectra of our compounds five to eight absorption bands arising from the ν(CH) stretching vibrations were observed.

The stretching vibrations of the aromatic ring are observed at $\tilde{\nu}$ = 1576 cm^{-1} and 1560 cm^{-1} in the noncoordinated bipyridine [13]. In the spectra of complexes these bands are observed at somewhat higher values of 1600 cm^{-1} and 1562—1572 cm^{-1} and besides these a new band appears in the spectra at 1496 cm^{-1}. Similar new band appears upon coordination of the pyridine molecule or molecules of 2-substituted derivatives of pyridine, respectively [14]. Due to coordination also the bands arising from ν(C—C) and ν(C—N) stretching vibrations are shifted to higher values of wavenumbers. Several bands appear in the spectra of our compounds in the region below 1400 cm^{-1} which can be attributed to various types of stretching and deformation vibrations of coordinated molecules of bipyridine. The positions of these bands are displayed in Table 2 together with the tentative assignment made on the basis of comparison with the spectra of noncoordinated molecule of bipyridine and published data [13, 14].

In the spectra of the prepared compounds are present also bands at 440 cm^{-1} and in the region 280—284 cm^{-1}. These absorption bands are absent in the spectrum of free bipyridine and on the basis of published data these were assigned to the δ(MCC) and ν(MN) types of vibrations [15, 16].

The bands due to ν(OH) stretching vibrations of noncoordinated water molecules appear in the region 3480—3560 cm^{-1} and the bands due to δ(HOH) deformation vibrations are in the region 1630—1650 cm^{-1}.

In the UV part of the electronic spectra of the studied compounds (Table 3) two intense bands in the regions 32 000—35 000 cm^{-1} and 41 000 cm^{-1} were observed which may belong to internal ligand transitions of $\pi \rightarrow \pi^*$(I) and $\pi \rightarrow \pi^*$(II) types, respectively. Analogous bands were observed in the spectra of similar bipyridine complexes [16, 17], but the band corresponding to the $\pi \rightarrow \pi^*$(I) transition is usually split. In the spectrum of CB2AH a shoulder occurs on the higher frequency side. The appearance of such shoulder can be explained by the splitting of π- and π^*-orbitals of coordinated bipyridine molecules owing to the reduction of local symmetry, or as a consequence of nonequivalency of the bipy ligands. The bands in the region 31 000 cm^{-1} may be also connected with the charge-transfer process of the M→L(bipy) (MLCT) type [18].

Table 3. Electronic Spectra of Complexes ($\tilde{\nu}$/cm^{-1})

Complex			bipy	Assignment
NB3AH	NB2AH	CB2AH		
		46600		$\pi \rightarrow \pi^*$(II)
40900	41840	42480	42400	$\pi \rightarrow \pi^*$(II)
			41200	$\pi \rightarrow \pi^*$(II)
35040	35560	35720	35400	$\pi \rightarrow \pi^*$(I)
32300	32400	31800		$\pi \rightarrow \pi^*$(I)
31100	31500	30700		$\pi \rightarrow \pi^*$(I)
18880	18560			$^3A_{2g} \rightarrow {}^3T_{1g}$(F)
		15360		$^2E_g \rightarrow {}^2T_{2g}$
12720	11200			$^3A_{2g} \rightarrow {}^3T_{2g}$(F)
11700	12900			$^3A_{2g} \rightarrow {}^1E_g$(D)
12720	11200	15360		10 Dq
≈ 840	≈ 860			B

The spectra in the visible part at $\tilde{\nu}$ = 11 000—30 000 cm^{-1} display characteristic absorption bands arising from $d \rightarrow d$ electronic transitions. In the octahedral complexes of Ni(II) appear three spin-allowed transitions $^3A_{2g} \rightarrow {}^3T_{2g}$(F), $^3A_{2g} \rightarrow {}^3T_{1g}$(F), and $^3A_{2g} \rightarrow {}^3T_{1g}$(P) and the spin-forbidden transition $^3A_{2g} \rightarrow {}^1E_g$(D). The transition $^3A_{2g} \rightarrow {}^3T_{1g}$(P) is fully overlapped by the charge-transfer bands, therefore in the spectra it is not observed. As can be seen from the measured spectra, in the case of NB3AH and NB2AH the positions of $^3A_{2g} \rightarrow {}^3T_{2g}$(F) and $^3A_{2g} \rightarrow {}^1E_g$(D) transitions are exchanged with each other, which is a consequence of variation of the ligand field force. The interpretation of the spectrum of NB2AH was made assuming that NB2AH exhibits analogous structure as CB2AH, *i.e.* pseudooctahedral coordination of the central atom by six nitrogen atoms, four from two bipyridine molecules and two from nitrogen atoms of bridging cyano groups. It is well known that cyano group bonded *via* carbon atom is a ligand of strong field. On the other hand, when it is bonded *via* nitrogen atom it behaves as a ligand of medium ligand field and its strength is under the strength of the coordinated ammonia molecule [19]. Consequently the force of the ligand field in the NB2AH complex is weaker than in the NB3AH and this corresponds to lower value of parameter 10 Dq. The bipyridine ligand exhibits such a strength of ligand field which corresponds in the Tanabe—Sugano diagram to crossing of the energetic levels of $^3T_{2g}$(F) and ^1E_g(D) states, and therefore a change in the order of the absorption bands is observed. The estimation of the Racah parameter B for this ligand is problematic as mutual interaction of these transitions occurs [20, 21].

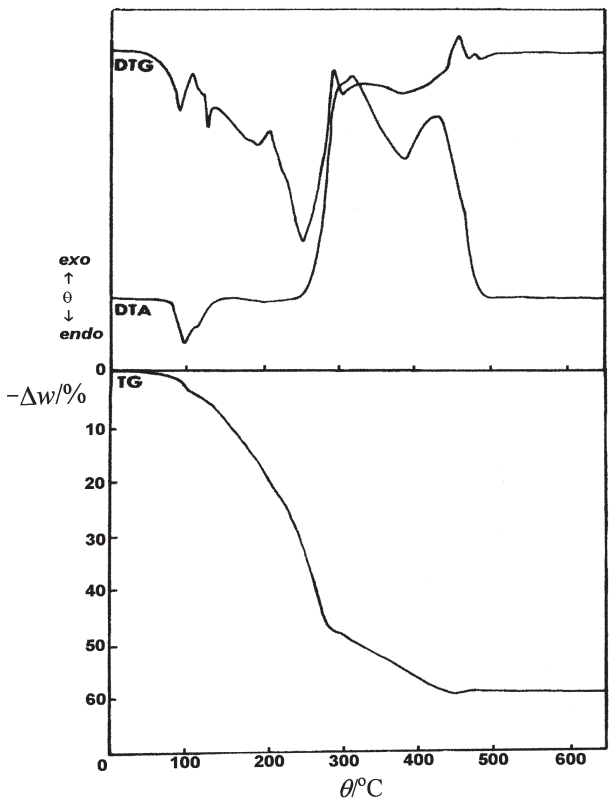

Fig. 1. Thermal decomposition curves for CB2AH.

The TG, DTA, and DTG curves of thermal decomposition of CB2AH are shown in Fig. 1. The thermal curves of NB2AH and NB3AH are analogous. The temperature ranges of decomposition reactions as well as the observed and calculated mass losses are gathered in Table 4.

The thermal decomposition of CB2AH starts at 60 ℃. The mass loss in the first step of thermal decomposition is 4.0 %, which corresponds to liberation of one molecule of water per formula unit (calc. 2.5 %). In the temperature range 130—140 ℃ the observed mass loss is 1.0 %. Optical observation using a heating plate has shown that CB2AH melts at 135 ℃. Both previous processes are endothermic. In the temperature range 140—302 ℃ a two-step process associated with a mass loss of 43.0 % occurs, which corresponds to the liberation of two moles of bipyridine (calc. 43.8 %). In the last stage of thermal decomposition an exothermic decomposition of cyanides and an oxidation of formed metallic copper take place; these are associated with a mass loss of 11.0 % (calc. 12.4 %). The final products are silver and copper(II) oxide. The total mass loss is 59.0 % (calc. 58.7 %). It was not possible to isolate the individual intermediates of thermal decomposition because these processes overlapped, which can be seen from the DTG curve, too.

NB2AH starts to decompose at 110 ℃. The first step of thermal decomposition is associated with a mass loss 3.0 %, which corresponds to liberation of one water molecule from the formula unit (calc. 2.5 %). In the temperature range 225—235 ℃ the mass loss is 1.5 %. External optical observation has shown that the NB2AH complex melts at the temperature 220 ℃. In the next step of thermal decomposition the mass is lowered by 22.0 %, which corresponds to liberation of one mole of bipyridine (calc. 22.0 %). All these processes are endothermic. In the temperature range 300—355 ℃ the mass loss is 7.0 % and this corre-

Table 4. Data on Thermal Decomposition of Complexes

Complex	θ/℃	Effect	$-\Delta w$(found) %	$-\Delta w$(calc.) %	Composition of the product
CB2AH	60—120	*endo*	4.0	2.5	$[Cu(bipy)_2][Ag(CN)_2]_2$
	130—140	*endo*	1.0	–	melting
	140—302		43.0	43.8	$Cu[Ag(CN)_2]_2$
	302—450	*exo*	11.0	12.4	CuO + 2Ag
			59.0	58.7	
NB2AH	110—200	*endo*	3.0	2.5	$[Ni(bipy)_2][Ag(CN)_2]_2$
	225—235	*endo*	1.5	–	melting
	240—295	*endo*	22.0	22.0	$[Ni(bipy)][Ag(CN)_2]_2$
	300—355	*exo*	7.0	7.3	$[Ni(bipy)](CN)_2$ + 2Ag
	355—400	*exo*	9.0	11.0	$[Ni(bipy)_{0.5}](CN)_2$ + 2Ag
	400—560	*exo*	16.0	16.0	NiO + 2Ag
			58.5	58.8	
NB3AH	40—102	*endo*	5.5	5.2	$[Ni(bipy)_3]_2[Ag(CN)_2]_3Cl \cdot 4H_2O$
	105—160	*endo*	4.3	4.2	$[Ni(bipy)_3]_2\ [Ag(CN)_2]_3Cl$
	170—182	*endo*	1.4	–	melting
	190—530	*endo, exo*	46.8	48.0	$[Ni(bipy)_{0.5}]_2(CN)_4$ + AgCl + 2Ag
	530—670	*exo*	13.0	13.1	2NiO + AgCl + 2Ag
			71.0	70.5	

sponds to liberation of one mole of dicyanogen (calc. 7.3 %), this process is exothermic. In the temperature range 355—400 °C the next mass loss is 9.0 % and this corresponds to liberation of 0.5 mol of bipyridine (calc. 11.0 %). This process is immediately followed by an exothermic process associated with a mass loss of 16 %, this may correspond to liberation of 0.5 mol of bipyridine, total decomposition of cyanides, and simultaneous oxidation of nickel to nickel(II) oxide (calc. 16.0 %). The total change of mass is 58.5 % (calc. 58.8 %). The final products of thermal decomposition are silver and nickel(II) oxide as determined by X-ray powder diffractometry.

In the first step of thermal decomposition of NB3AH a mass loss of 5.5 % corresponding to liberation of five molecules of water from the formula unit can be observed (calc. 5.2 %). In the next step of thermal decomposition the observed mass loss is 4.3 %, this value is consistent with the liberation of the remaining four water molecules (calc. 4.2 %). Both these processes are endothermic. Two endothermic peaks associated with a mass loss of about 1.4 % can be seen on the DTA curve at temperatures 170 °C and 182 °C. These two processes probably represent a phase transition followed by melting of the sample. Optical observation on heating plate indicated melting of the anhydrous NB3AH at 155 °C. In the temperature range 190—530 °C a mass loss of 46.8 % corresponding to five partially overlapped steps is observed, these can be explained as composed of liberation of five moles of bipyridine and one mole of dicyanogen originating from the decomposition of dicyanoargentate group (calc. 48.0 %). Total thermal decomposition of cyanides and simultaneous oxidation of nickel to nickel(II) oxide occurs in the final strongly exothermic step of thermal decomposition in the temperature range 530—670 °C. Nickel(II) oxide, metallic silver, and silver chloride were found by X-ray powder diffractometry to be the final products of the thermal decomposition. The total observed mass loss is 71 % (calc. 70.5 %).

The comparison of thermal analyses of all three complexes allows to conclude: endothermic dehydration is the first process in all complexes, this dehydration is a two-step process in the case of NB3AH; comparison of the starting temperatures of dehydration yields the following increasing order of stability: NB3AH, CB2AH, NB2AH; melting observed for all three samples is associated with a nonstoichiometric mass loss from 1.0 to 1.5 %; the liberation of bipyridine molecules occurs in several overlapped processes; the final products of thermal decomposition are oxides NiO and CuO, respectively, and silver as well as AgCl in the case of NB3AH.

The comparison of the thermal stability of the studied complexes with analogous ones containing *N*-donor ligands like ammonia, ethylenediamine, and phenanthroline yields the next increasing order of stability with respect to liberation of these ligands [22—24]: NH_3, en, bipy, phen.

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